THE BOEING COMPANY
Aerospace Group

IDENTIFYING OPTIMUM PARAMETERS OF HOT EXTRUSIONS

Contract NAS 7-276

Prepared for

Chief, Materials Research Branch
National Aeronautics & Space Administration
Headquarters
Washington, D. C.

Progress Report No. 14
14 July 1967 to 17 October 1967

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ABSTRACT

Further testing of the effect of annealing on the strength of extruded MgO has been conducted. An insufficient number of satisfactory samples was available for making firm conclusions; however, results appear to be consistent with the hypothesis that work hardening protects surfaces from minor flaws. Somewhat lower relative annealed strengths are observed with finer grain sizes while somewhat higher relative annealed strengths are observed with larger grain sizes. Possible causes of this effect are discussed.

Limited ductility is observed in testing extruded MgO (derived from fused single crystals) at 1540°C. Fracture strengths are not much lower than those at 1315°C or room temperature. Possible reasons for this fact are discussed. Fracture appears to originate at or near triple points, but propagates mostly by cleavage at this temperature, as was the case at 1315°C.

Comparison of grain sizes just before and after extrusion corroborate previous evidence that the transverse grain size is determined primarily by physical reduction of grains in proportion to the reduction ratio.

Several instrumented cans with a number of different billets are now nearly ready for extrusion which should be performed before the end of October.

CONTENTS

WORK ACCOMPLISHED

A. BILLET PREPARATION

1. Billet Fabrication

Billet fabrication was continued using the procedure of Appendix 1 with pressing conditions modified as shown in Table I. Table I also shows firing and resultant density data.

Planned extrusion at lower temperatures allow $MgAl_2O_4$ to be considered where can, space and other factors permit. Therefore, sample powder* (2-3 micron crystal size) was vacuum hot pressed as shown in Table I. The first two attempts failed due to die breakage. Since the material showed heavy outgassing, pressure was applied more slowly to allow gases to escape. This proved successful; however, most of the hot pressed billets developed blisters during subsequent firing (some quite severe). Cutting a 1" cube from a 1.5" diameter billet revealed a large black core left after the slow 2800°F(1540°C) firing.

2. Preparation and Receipt of Other Billets

CaO crystals were received** for single crystal and forged specimens. The latter were readily forged at temperatures of about 1600°C with about 5000 psi.

ZrO_2 (Y_2O_3 stabilized)*** samples were received (courtesy of C. Armstrong of Boeing).

Other billets were prepared from materials on hand as shown in Table I.

B. EXTRUSIONS

Late delivery of some components has delayed the first set of extrusions; however, most are expected to be run before the end of October.

C. MATERIAL ANALYSIS

1. Effect of Surface Condition on Annealed Strengths

Specimens were cut from extruded MgO crystals then annealed in air for 1 hour at 2600°F(1425°C) or 2800°F(1540°C). These were then tested at room

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*Courtesy of Dr. J.G. Lindsay of Aluminum Laboratories-Aluminum Co. of Canada, Ltd.
**Muscle Shoals Electrochemical Corp., Tuscumbia, Ala.
***Zircoa; Solon, Ohio.

temperature in 3 point bending (0.5" span) with the bar surfaces: (a) in the as-fired condition, (b) with subsequent sanding (280, 400, then 600 grit dry sanding), (c) chemically polished 5 minutes in boiling H_3PO_4 (approximately 1.3 gm/cc density - boiling point about 150°C). Such "crystal" specimens were used because they avoid any complications of "gaseous impurities" often found in specimens from hot pressed material even though their limited supply restricted testing. Resultant strength versus grain size data is shown in Figures 1 and 2.

Examination showed that fracture origins of chemically polished specimens were exclusively from the tensile surface or somewhere in a grain along the tensile surface, while sanded specimens almost always had internal fracture origins in agreement with previous results. The as-fired specimens again showed a preference for surface origins, but not as clear as chemically polished specimens. Some fractures again showed slip band intersections or terminations at the origin. The fracture of the weakest sanded specimen in Figure 1 suggested an origin from a surface flaw.

Occasional grain boundary surfaces are exposed on such room temperature fracture surfaces. Some of these have shown slip bands; however, these have been difficult to photograph because of the grain relief. One example of such a boundary surface with more easily photographed slip bands was observed and is shown in Figure 3.

2. Strength of Extruded MgO at 2800°F(1540°C)

Extruded MgO specimens were tested at 2800°F(1540°C) in air with 3 point bending utilizing 0.1" diameter sapphire loading points (0.5" span), Al_2O_3 supports, and Pt-40% Rh resistance windings. Only extruded MgO crystals were used to avoid degradation and hence non-intrinsic results commonly found in extruded MgO derived originally by hot pressing. All specimens were tested after chemical polishing.

Six of eight specimens showed yielding before fracture (see Figure 4), some with subsequent macroscopic deformation as shown in Figure 5A. Plastic deformation is also indicated by the apparent fracture stress (calculated bend strength neglecting plastic flow) being substantially higher than the yield stress for most of the specimens (see Figure 4).

Fracture surfaces tended to be rougher than those found in room temperature testing, but the general area of fracture origin could be found. The origin areas consisted mostly or exclusively of grain boundary surfaces with the remainder of the fracture being almost exclusively cleavage as shown in Figures 5B and C. The grain boundary surface or surfaces in the origin area made it difficult to determine a specific origin; however, observations indicate that triple points are often at or near the origin.

3. Grain Size Analysis

Grain size and other data from various stalled or aborted extrusions are shown in Table 2.

DISCUSSION

A. EFFECT OF SURFACE CONDITION ON STRENGTH

Not enough extruded crystal specimens were available to provide a large population, so firm conclusions cannot be drawn from these tests. However, the results are consistent with the hypothesis proposed in the last report (No. 13) that sanding protects the surface due to the apparent work-hardening of the surface. Only one sanded specimen deviated significantly below the strength curve previously established for extruded MgO, and the fracture surface indicates this specimen may have failed from a flaw.

Two other observations were made which are also consistent with earlier annealing data. First, chemically polished specimens appear to be more likely to show greater drops in strength. This might result from some preferential attack of grain boundaries due, for example, to impurities. The second observations is that finer grain sizes are more likely to deviate below the $G^{-1/2}$ strength curve, while large grain sizes often deviate above the curve. The data from these tests does not clearly demonstrate the usual decrease of strength with increasing grain size. However, the definite variation of strength with grain size in other tests, and the following possible variables suggest other factors in these tests. The apparent greater relative strengths at larger grain sizes could arise from:

(a) Substructure. It has previously been observed that some substructure exists in some grains, with this appearing most common in larger grains. If this is not consistently detected and such structure effects strengths (for example as sources or impediments for dislocations), then the observed grain size would be incorrectly large.

(b) Increased Texture. Annealing tests have indicated that texture may increase with annealing and grain growth. Thus larger grain size specimens may have less misorientation between grains and hence higher strengths.

Possible reasons for the apparent lower strength at finer grain size have been difficult to ascertain. Impurities may be one reason. Since all of the crystals are similarly extruded and annealed, finer grain sizes must be predominately due to different impurities, substructure, or imperfections in the starting crystals. All of these, especially impurity type, state, and distribution can vary substantially in MgO crystals. Resultant greater impurity content or more unfavorable distribution (e.g. at grain boundaries) could then lead to disproportionate greater average weakening of finer grain specimens.

B. HIGH TEMPERATURE STRENGTH AND FRACTURE

Day and Stokes[1,2,3] have previously reported that recrystallized MgO crystals were ductile in tension above 1700°C when tested at a strain rate of approximately 5×10^{-4} sec^{-1}, with higher strain rates increasing the brittle-ductile transition temperature. The indicated ductility at 1540°C with higher strain rates indicates that the texturing of extrusion may lower the ductile brittle transition temperature. This is not surprising in view of the fact that texturing would reduce grain misorientation and thus the propensity for both grain boundary crack nucleation and sliding, either of which can cause brittle failure. Day and Stokes[1,2] single crystal yield stress of 3500-4000 psi in the range 1500-1600°C also appears to generally agree with observed values for the extruded recrystallized "crystal" specimens.

Previous testing had shown that the suggested functional relationship between strength and grain size were approximately the same at room temperature and 2400°F(1315°C), with several specimens showing elevated temperature fracture strengths substantially above room temperature strengths for the same grain size. Fracture strengths of specimens having some ductility at 2800°F(1540°C) average only slightly lower as shown in Figure 4. This figure also shows that fracture stresses of specimens failing without macroscopic yielding appear to agree well with the yield stress levels, suggesting fracture just at yield for these specimens. Though, enough specimens have not yet been available to clearly establish a functional relationship, both yield and "ductile" fracture stresses also appear to be consistent with an inverse square root grain size relationship.

The occurrence of the same or greater strength at 2400°F(1315°C) than at room temperature, and the same or only slightly less strength at 2800°F(1540°C) is not unreasonable. Though both intrinsic bond strength and yield stress decrease continuously with temperature, other changes in dislocation behavior occur which may counteract such decreases at intermediate temperatures. Before macroscopic yielding occurs, slip bands become more diffuse with increasing temperature which should reduce stress concentrations at dislocation pile-ups. This may reduce, cancel, or possibly overcome the above decreases over some temperature range. After macroscopic yielding occurs, work hardening can begin to occur, which also limits the drop in strength due to falling yield stress.

The origin of fracture from grain boundary surfaces, probably at or near triple points is consistent with earlier data at 2400°F(1315°C), as is the predominance of cleavage on the rest of the fracture. This is in contrast to the mostly intergranular fracture of hot pressed bodies which probably arises from impurities, especially "gaseous" impurities, left from hot pressing.

C. GRAIN SIZE

The data of Table 2 shows that higher billet density is the most important factor in yielding larger grain sizes after heating for extrusion. This is in agreement with previous data (Appendix 6 of Interim Report III), as is the indication that fabrication with LiF, and higher initial firing temperatures increase the grain size.

Extrusion of bodies with such grains would reduce the grain diameter in the same ratio as the cross sectional reduction ratio. This would then determine the resultant transverse grain size, unless recrystallization further altered transverse grain diameters. Thus extruded grain sizes would be 1/3 those of Table 2 for the 9 to 1 reduction ratio used in almost all extrusions. Since extruded grain sizes have been in the range of one third of the unextruded grain sizes in Table 2, and extruded grain size variations have tended to follow the same parameters as have the unextruded billets; these results suggest that reduction ratio and not recrystallization is the most important factor (besides billet parameters) in the resultant grain size. This agrees with photos of earlier extruded billets indicating grain elongation with recrystallization primarily active in forming new transverse boundaries (perpendicular to the grain and extrusion axis).

SUMMARY & CONCLUSIONS

Extruded (recrystallized) MgO crystals exhibit some ductility at 1540°C, but show limited decreases in fracture strengths from room temperature levels.

Tests of annealed specimens, though not complete, appear to be consistent with the previous hypothesis of work hardened surfaces (from sanding) providing some protection from sub-critical surface flaws. Higher impurity content was suggested as a contributing factor to relatively lower annealed strengths at finer grain sizes, while substructure and increased orientation were suggested as causes of relatively greater annealed strengths at larger grain sizes.

Comparison of grain sizes just before and after extrusion indicates that physical reduction of grain diameters in proportion to the reduction ratio is the primary factor (for given billet parameters) in extruded transverse grain sizes.

FUTURE WORK

At least two, and probably four extrusions will be run before the end of October. These are expected to provide key information on the benefits to be obtained from both insulating can extrusions and from prior hot forging of billets.

Another series of extrusions is planned for November or December, one of which will probably be a fluid extrusion.

REFERENCES

1. R. B. Day and R. J. Stokes, "The Mechanical Properties of MgO as a Function of Temperature", J. Am. Ceram. Soc. 42 (21), pp. 72-80, February 1966.
2. R. B. Day and R. J. Stokes, "Mechanical Behavior of Polycrystalline MgO at High Temperatures", J. Am. Ceram. Soc. 49, (7), pp. 345-54, July 1966.
3. R. B. Day and R. J. Stokes, "Grain Boundaries and the Mechanical Behavior of Magnesium Oxide", Materials Science Research, Vol. 3 (Ed. by W.W. Kriegel and H. Palmour III) pp. 355-86, Plenum Press, New York, 1966, 611 pages.

TABLE I. BILLET FABRICATION

Billet			Pressing[1]				
Number	Composition	Dia. (in)	Pressure Applied at:	Held at:	For (min)	Fired to:[2]	Density[3] (gm/cc)
M-6-7	Mallinckrodt MgO	2.0	2350°F(1285°C)	2400°F(1315°C)	20	2800°F(1540°C)	3.55
-8	Fisher MgO	1.0	↓	↓	↓	↓	3.55
-9	Fisher MgO	2.0	↓	↓	↓	↓	3.57
-10	Mallinckrodt MgO	2.0	↓	↓	↓	↓	3.55
-11	Mallinckrodt MgO	2.0	↓	↓	↓	↓	3.55
-12	Fisher MgO	2.0	↓	↓	↓	2800°F(1540°C)	3.57
-13	Fisher MgO	1.5	↓	↓	↓		
-14	Fisher MgO	1.5	↓	↓	↓		
-15	Mallinckrodt MgO	1.5	↓	↓	↓		
-16	Fisher MgO	1.5	↓	↓	↓		
-17	Mallinckrodt MgO	1.5	↓	↓	↓		
-18	Fisher MgO	1.5	↓	↓	↓		
-19	Mallinckrodt MgO	1.5	↓	↓	↓		
-20	Fisher MgO	1.5	↓	↓	↓		
-21	Mallinckrodt MgO	1.5	↓	↓	↓		
-22	Mallinckrodt MgO	1.5	↓	↓	↓		
-23	Fisher MgO	1.5	↓	↓	↓		
-24	Mallinckrodt MgO	1.5	↓	↓	↓		
-25	Mallinckrodt MgO	1.5	↓	↓	↓		
-26	Mallinckrodt MgO	1.5	↓	↓	↓		
-27	Fisher MgO	1.5	↓	↓	↓		
-28	Mallinckrodt MgO	1.5	↓	↓	↓		
-29	Fisher MgO	1.5	↓	↓	↓		
-30	Mallinckrodt MgO	1.5	↓	↓	↓		
M-7-1	Fisher MgO	1.5	↓	↓	↓		
-2	Fisher MgO	1.5	↓	↓	↓		
-3	Fisher MgO	1.5	↓	↓	↓		
-4	Fisher MgO	1.0	↓	↓	↓		
-5	Fisher MgO	1.0	↓	↓	↓		
-6	Fisher MgO	1.0	↓	↓	↓		

TABLE I. (CONTINUED)

Billet			Pressing[1]					
Number	Composition	Dia. (in)	Pressure Applied at:		Held at:	For (min)	Fired to:[2]	Density[3] (gm/cc)
M-7-7	Mallinckrodt MgO	1.0						
-8	Mallinckrodt MgO	1.0						
-9	Mallinckrodt MgO	1.0						
A-1-19	Ruby	0.75						
C-1-13	CaO Crystal							
S_{ma}-1-4	Spinel		2400°F(1315°C)		Die Broke			
-5					Die Broke			
-6		1.5		(4)	2500°F(1370°C)	120		
-7		1.5		(5)	2460°F(1350°C)	30	2800°F(1540°C)	2.70
-8		1.5			2500°F(1370°C)	180	2800°F(1540°C)	3.42
-9		1.0			2500°F(1370°C)	120		
Z-1-6	ZrO_2 (CaO Stabilized)							
Z-2-1	ZrO_2 (Y_2O_3 Stabilized)							

(1) Pressed at 5000 psi unless otherwise noted.
(2) On Firing Schedule A (Appendix 2).
(3) After firing. Average error ±0.01 gm/cc.
(4) Pressed at 4000 psi.
(5) Pressed at 3300 psi.

TABLE 2 - BILLET GRAIN SIZE AFTER HEATING FOR EXTRUSION

Billet	Billet Firing °C	Extrusion Heating °C[1]	Dia. (in)	Density, gm/cc Before Heating	Density, gm/cc After Heating	Final Grain Size (microns)	
M-1-8 (LiF)*	1565	2200	1.5	3.53	3.58	163	
M5N-1-1 (LiF)	1565	"	"	3.27		100	Extrusion MgO-7
M1A-1-9 (Lif)	1380	"	"	3.50		400	
M-2-20	1315	"	"	3.59		76	
M-3-1	1315	"	"	3.54		65	
M-3-2	1315	"	"	3.56		50	Extrusion MgO-10
M-2-7	1565	"	"	3.59		90	
M-2-21	1315	"	"	3.58		64	
m-1-1	-	"	"	1.5		38	
OP-211	-	"	0.75	3.58	3.58+[3]	Outside 3000 Center (98)	
M-3-25	1205	" (2)	1.0	3.38	3.39	38	
M-3-17	1315	" (2)	1.5	3.52	3.53	33	
M-3-13	1205	" (2)	1.5	3.56		70	Extrusion MgO-16
M-3-21	1205	" (2)	1.5	3.31	3.35	36	
M-3-24 (LiF)	1205	" (2)	1.5	3.27		56	

TABLE 2 - CONTINUED

Billet	Billet Firing °C	Extrusion Heating °C(1)	Dia. (in)	Density, gm/cc Before Heating	Density, gm/cc After Heating	Final Grain Size (microns)	
M-3-11	1315	2200	1.0	3.59	3.58+(3)	191	
M-3-22	1205	"	1.0	3.60	3.58+(3)	185	
M-3-16	1315	"	1.5	3.59	3.58+(3)	507	Extrusion MgO-17
M-3-20	1205	"	1.5	3.58	3.58+(3)	160	
M-3-6	1315	"	2.0	3.58	3.58+(3)	162	
m-1-4	-	"	0.9	1.5	3.56	55	
M-1-17	1565	"(2)	1.5	3.54	3.58+(3)	133	
M-3-12	1315	"(2)	1.5	3.58		102	
M2N-1-4	1565	"(2)	1.5	3.47	3.49	100	
M5N-1-3	1565	"(2)	1.5	-	3.41	58	Extrusion MgO-20
M1A-1-5	1315	"(2)	1.5	3.55	3.55	107	
M5A-1-3	1565	"(2)	1.5	3.43		40	

*(LiF) means the billet was hot pressed with 2 w/o LiF.

(1) Optical reading at rear of can just before dropping billet.

(2) Central area of TZM shell melted indicating temperatures above 2200°C.

(3) Estimated near theoretical density from translucency.

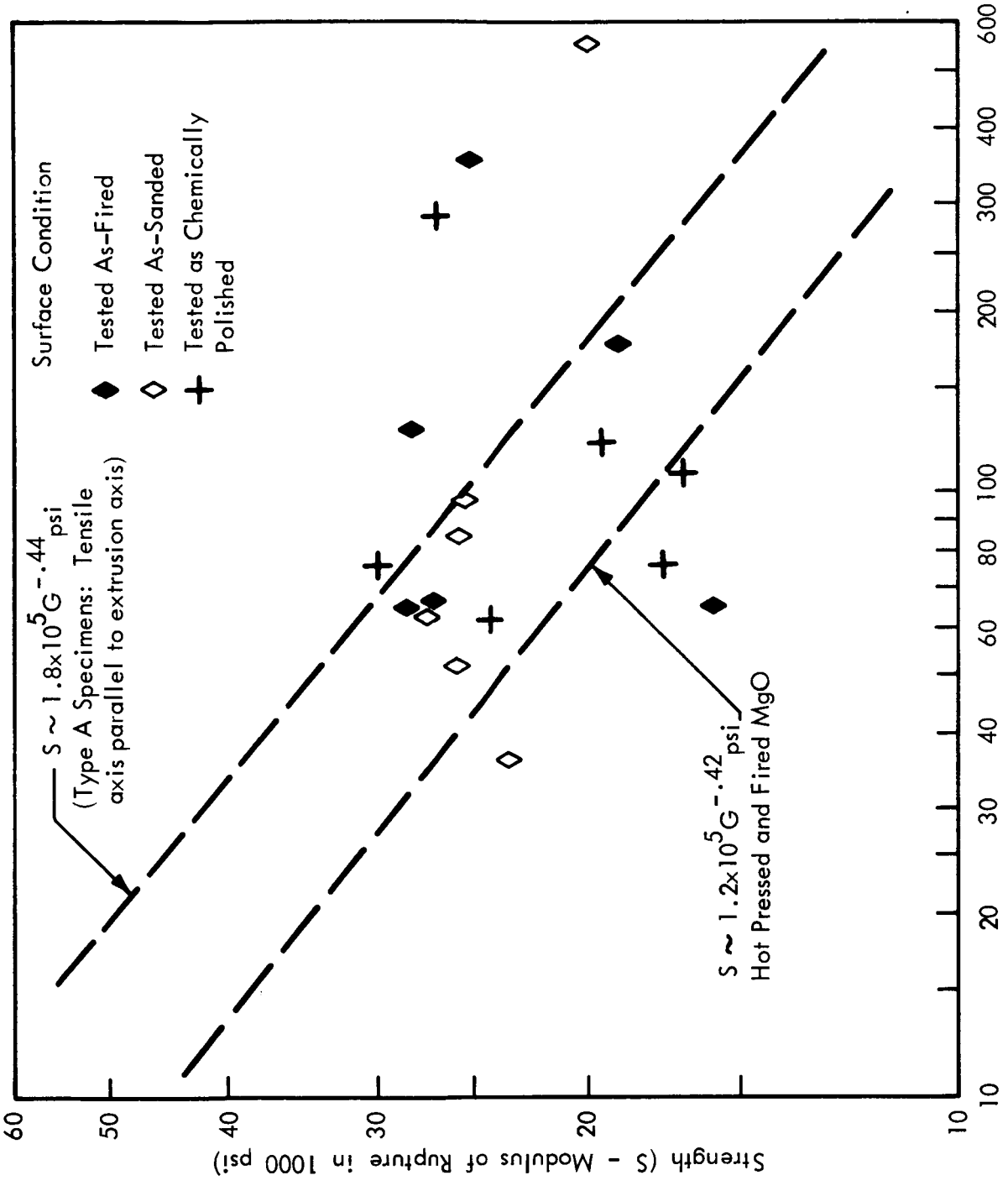


FIGURE 1. ROOM TEMPERATURE STRENGTH VERSUS GRAIN SIZE OF EXTRUDED MgO ANNEALED 1 HOUR AT 2600°F(1425°C) IN AIR

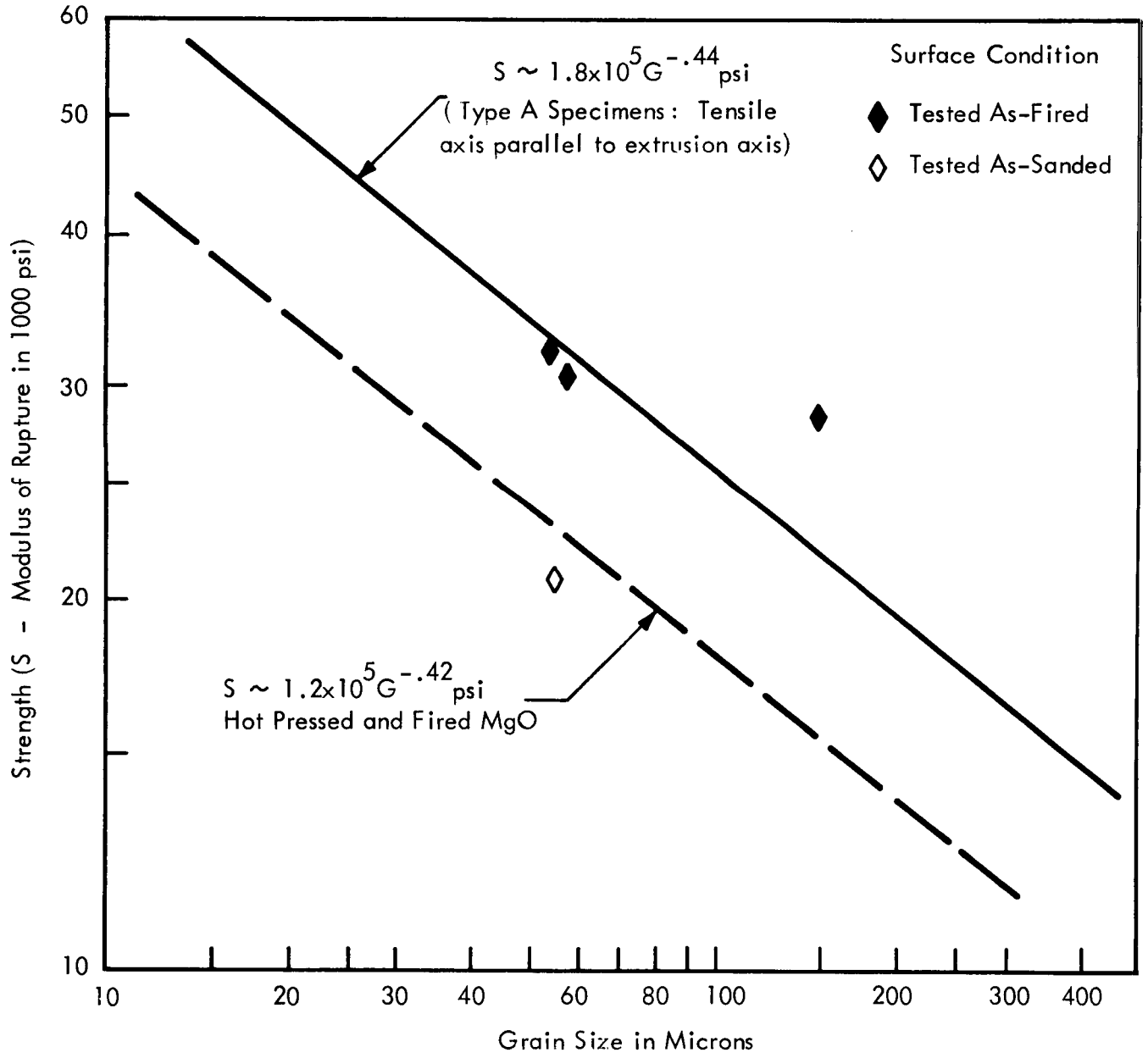


FIGURE 2. ROOM TEMPERATURE STRENGTH VERSUS GRAIN SIZE OF EXTRUDED MgO ANNEALED 1 HOUR AT 2800°F(1540°C) IN AIR

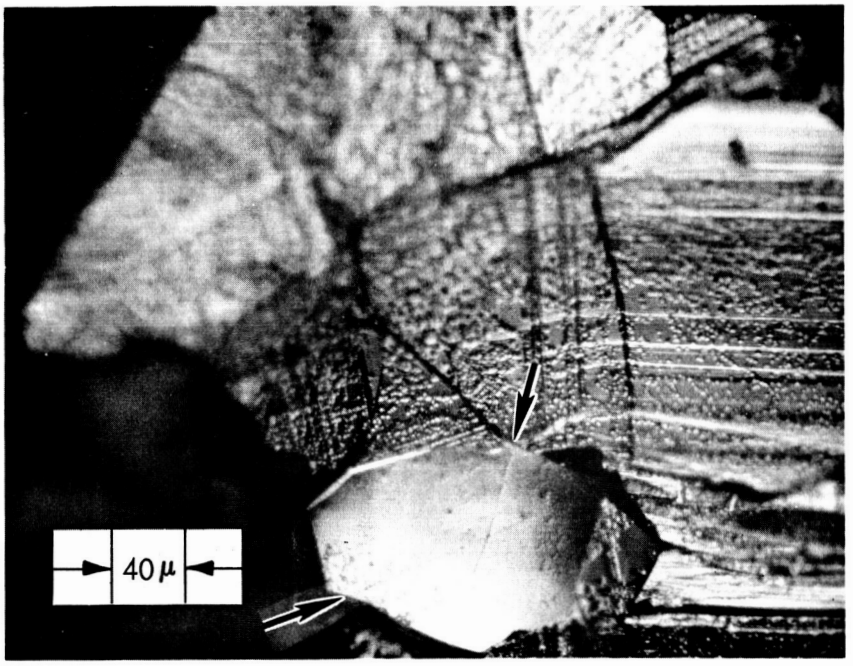


FIGURE 3. SLIP BANDS ON GRAIN BOUNDARY SURFACE EXPOSED BY ROOM TEMPERATURE FRACTURE (SEE ARROWS). SPECIMEN M-f-4_{A4}.

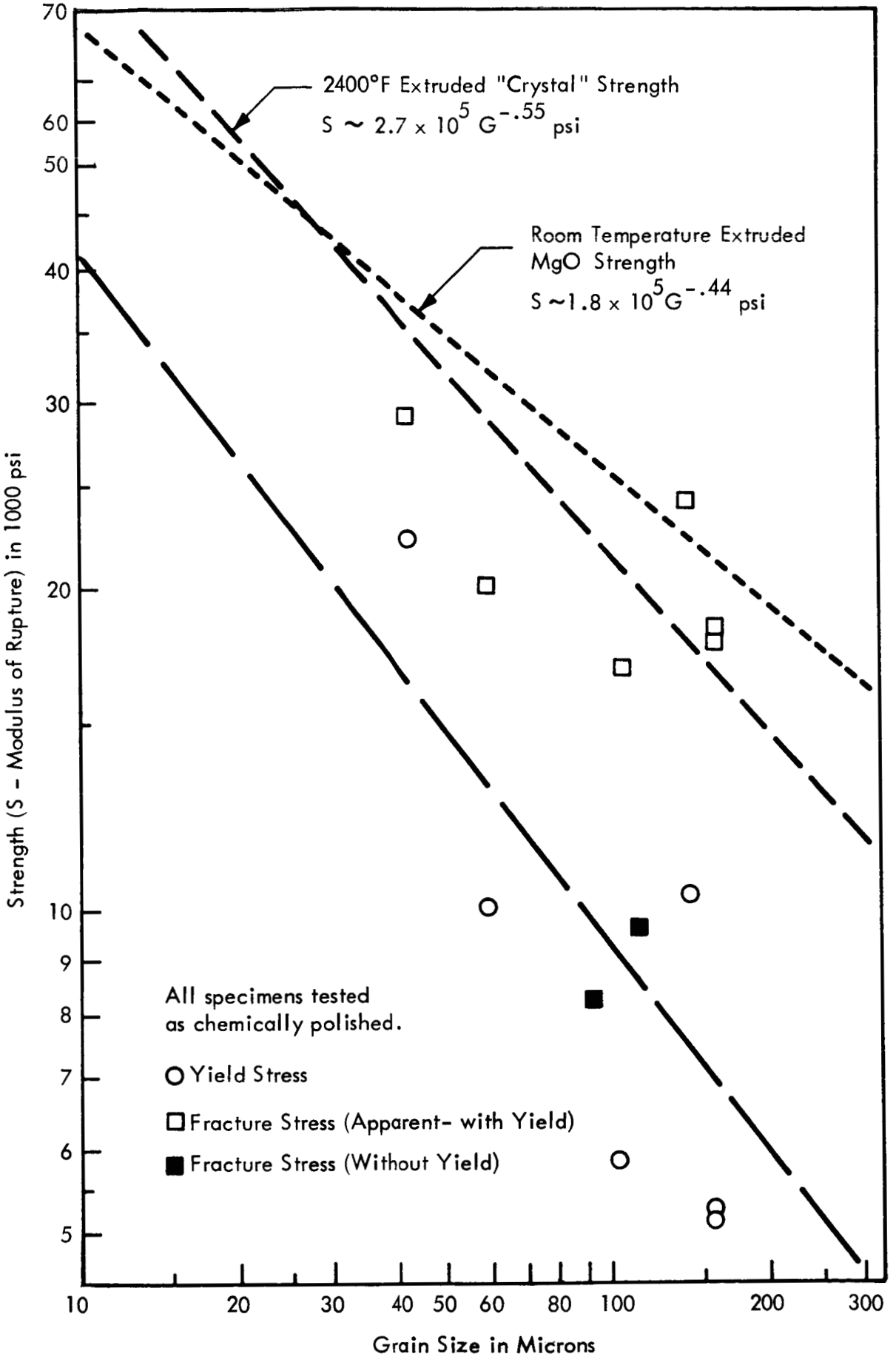


FIGURE 4. STRENGTH OF EXTRUDED MgO CRYSTALS AT 2800°F(1540°C)

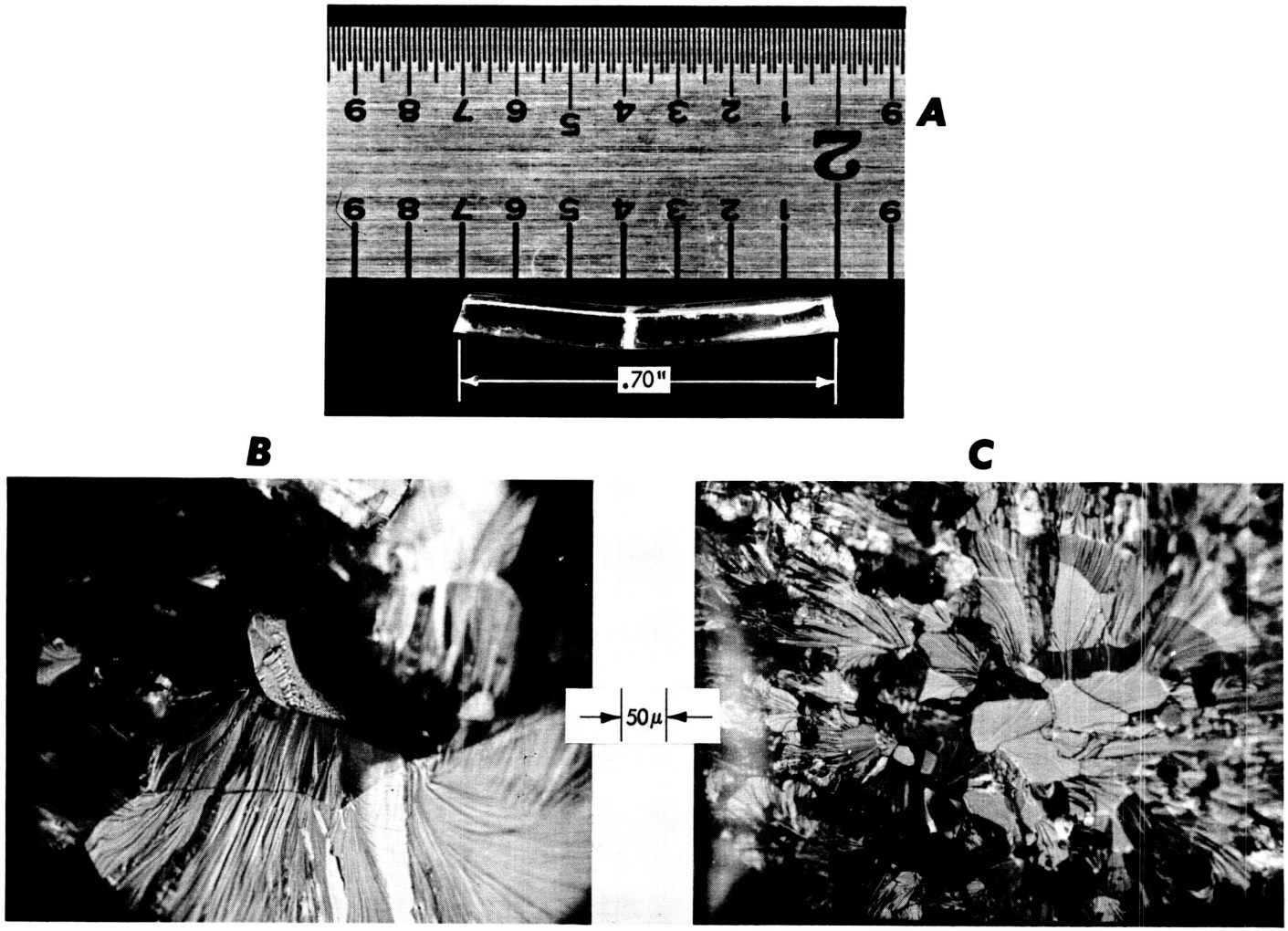


FIGURE 5. 2800°F(1540°C) FRACTURE OF EXTRUDED MgO CRYSTALS. (A) MACRO PHOTO OF SPECIMEN M-f-149 AT FRACTURE. (B) FRACTURE ORIGIN OF M-f-149. (C) FRACTURE ORIGIN OF M-f-12_{A1a}.

APPENDIX 1

BILLET VACUUM HOT PRESSING PROCEDURE B (WITHOUT LiF)

1. Powder is directly loaded into the die from sealed bottles, without any prior milling unless milling was previously used to mix alloy agents. Pyrolytic graphite spacers are used between the rams and the specimen when graphite dies are used.

2. The powder is cold pressed at 1000-2000 psi.

3. The die is placed in the vacuum hot press which is pumped down to a chamber pressure of 10^{-4} to 10^{-5} torr in about one hour.

4. After at least 2 hours at 10^{-4}-10^{-5} torr the die is heated to 1650°F(900°C) in about 30 minutes. Temperatures are measured optically at the approximate center of the side of the die.

5. Starting at 1750°F(950°C) the ram pressure is built up to 5000 psi over a period of about 2 minutes.

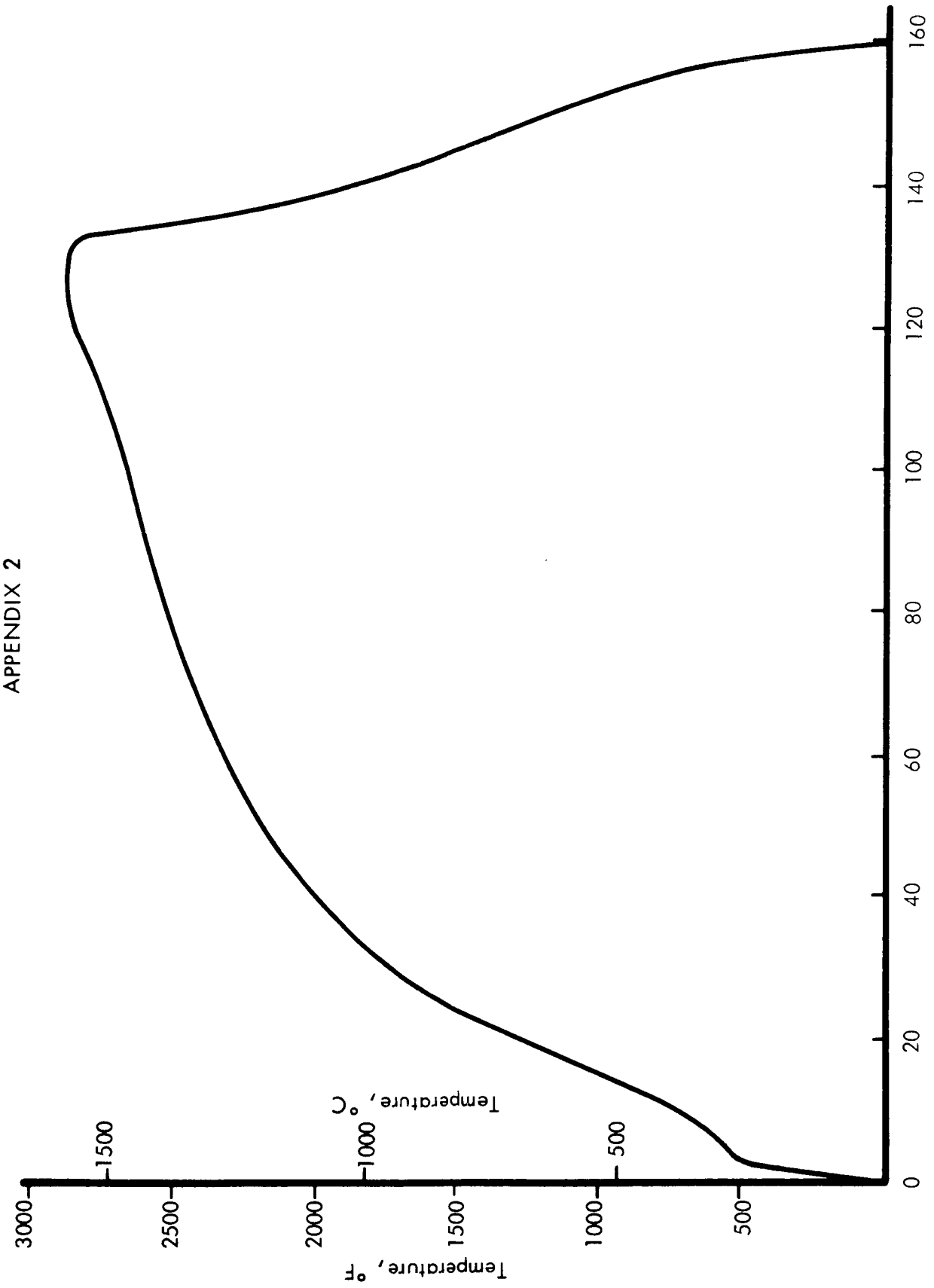
6. A temperature of 2400°F(1315°C) is then reached in about 20 minutes, while maintaining the ram pressure at 5000 psi.

7. Pressing conditions of 2400°F and 5000 psi are held for 15 minutes with vacuum chamber pressure averaging about 10^{-2}torr.

8. The induction heating power is shut off and the ram pressure released over a period of about 1 minute.

9. The die is removed from the vacuum hot press after cooling for two to four hours.

10. The specimen is ejected from the die at a temperature of 750°F(400°C) or less.



FIRING SCHEDULE A